

Near-Infrared Spectroscopic Determination of Carbon, Total Nitrogen, and Ammonium-N in Dairy Manures¹

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ABSTRACT

The objective of this study was to investigate the feasibility of using near-infrared reflectance spectroscopy (NIRS) to determine nutrient concentrations in dairy manures. We assayed diverse dairy manures ($n = 107$), collected from dairy farms in the northeastern United States (CT, MD, NY, PA, and VA) by conventional means and NIRS for total C, total N, $\text{NH}_3\text{-N}$, moisture, P, K, and pH. Samples were scanned from 400 to 2498 nm in polyethylene bags on a FOSS-NIR-Systems Model 6500 scanning monochromator equipped with a sample transport device. We developed calibrations using a one-out cross validation procedure under partial least-squares regression. Preliminary results showed that eight samples were outliers either because of inaccurate conventional analysis or because they were uncharacteristic (i.e., two samples had moisture content below 72%, while all others were above 78%). These outliers were removed from further consideration. Final calibration results with the remaining 99 samples demonstrated that NIRS can accurately determine the moisture ($r^2 = 0.945$, root mean squared deviation or RMSD = 1.0%), total C ($r^2 = 0.950$, RMSD = 0.40%), total N ($r^2 = 0.956$, RMSD = 0.030%), and $\text{NH}_3\text{-N}$ ($r^2 = 0.967$, RMSD = 0.013%) concentrations, but not P or K concentrations in dairy manures. In conclusion, NIRS was shown to be a viable alternative to conventional analysis procedures for determining moisture, total C, total N, and $\text{NH}_3\text{-N}$ in a very diverse set of dairy manures.

(Key words: near-infrared, manure, carbon, nitrogen)

Abbreviation key: NIR = near-infrared, NIRS = NIR reflectance spectroscopy, PLSR = partial least-squares regression, RMSD = root mean squared deviation.

INTRODUCTION

Over the last few decades, near-infrared reflectance spectroscopy (NIRS) has risen as an alternative method of analysis for rapidly determining the composition of a wide variety of materials ranging from forages (5), grains (20), and food products (13) to the octane content of gasoline (8). Based on the relationships between spectral and compositional properties of a set of samples, NIRS can accurately and rapidly determine the composition of samples (12), while greatly reducing the waste associated with conventional analysis systems such as those for Kjeldahl N and ammonium-N (4).

Because of increasing concern for the potential pollution from farm manures, rapid, robust methods of analysis for manure nutrient concentrations are needed (22, 24), including procedures that can be used on the farm. At the present time, most manures are analyzed by conventional wet chemical methods, such as the Kjeldahl procedure for total N or ammonium-N (4) or by combustion techniques for total C or N (2). These procedures, while accurate, can be time consuming and expensive, and they generate chemical wastes. A small amount of work by NIRS has been done on cattle manure (3), manure composts (9), and hog manure (11), but its potential for measuring such materials remains largely unexplored. Near-infrared reflectance spectroscopy generates no wastes and can provide concentration estimates for multiple components in a few minutes once calibrations have been developed for the components of interest.

At the present time, several methods of determining manure ammonium-N concentrations are available for on-farm testing of manures. These include the Quantofix-N-Volumeter (10) and Agros N meter (25), which utilize the reaction of hypochlorite (ClO^-) with ammonium-N, a reflectometer that uses colorimetric test strips (25), conductivity pens and meters (19), and hydrometers (21). While some of these methods are quite accurate, they generally only determine the ammonium-N content of the manure, and, therefore, are of little or no value in providing information on the C and organic N fractions. Unfortunately, a complete N profile of manure is necessary to predict the N available for plants. While no small, inexpensive, near-infrared

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(NIR) spectrometers or meters are presently available for on-farm evaluation of manures, their development in other areas—such as those that determine body fat in humans (1)—shows such an instrument could be possible.

The objective of this study was to investigate the feasibility of using NIRS to determine the nutrient composition of dairy manures.

MATERIALS AND METHODS

Samples and Compositional Determinations

Dairy manure samples ($n = 107$) were collected from farms in Connecticut, Maryland, New York, Pennsylvania, and Virginia in the fall of 1998. Samples were collected from manure storage facilities and ranged from slurries with moisture contents as high as 98.6% to solids with moisture contents as low as 61.4% (70°C DM). Approximately 9 to 10 L of each manure was collected and mixed, and subsamples were taken for various analyses. All samples were stored at 4°C from the time of arrival at the laboratory to the time of analysis. Previous work showed that samples can be stored for several weeks in this manner with little or no change in the N composition (23). Analysis for total C, total N, $\text{NH}_3\text{-N}$, P, K, and moisture (DM content) were performed at the University of Maryland (College Park, MD) Soil Testing Laboratory. Total C and organic N were determined by combustion on samples dried at 70°C (2). Ammonium-N was determined by distillation (4); total N by the addition of organic N and ammonium; P, and K by perchloric and nitric acid digestion (18); and DM (loss of volatiles) by oven drying at 70°C to a constant weight (all determined with nondried samples). Because of the nature of the assays used, organic N determinations may include some residual nonvolatilized NH_3 , and DM determinations include loss of volatiles such as NH_3 . Also, some residual moisture would still be present. All assay values were computed on an as-is basis.

For comparison, we also analyzed all samples using six quick tests presently marketed for manures. Detailed descriptions of these tests and their accuracy are given in Van Kessel and Reeves (24).

Statistical Analysis

Descriptive statistics and regression analysis were performed using SAS version 6.19 (17).

Near-Infrared Spectroscopy

Samples were scanned in triplicate from 400 to 2498 nm with spectra collected every 2 nm on a FOSS-NIR-

Systems model 6500 scanning monochromator (FOSS-NIRSystems, Silver Spring, MD). The spectrometer was equipped with a sample transport device that allows a polyethylene bag approximately 4 cm wide \times 15 cm long to be scanned while moving vertically. Spectra were collected from 400 (visible) to 1098 (short-wave NIR) nm with a Si detector and from 1100 to 2498 (NIR) with a PbS detector. Sixty-four co-added scans (sample scanned from 400 to 2498 nm 64 times and results added to produce one spectra) were collected for each sample. Samples were scanned as obtained, with no grinding or sample preparation other than mixing. Sample temperature at the time of scanning was approximately 4°C. Samples were scanned at 4°C to avoid loss of volatiles and changes in the sample that might occur during warming. We thoroughly mixed samples by shaking or stirring before placing a subsample into the polyethylene bags.

Calibration Development

Near-infrared calibrations were performed by partial least-squares regression (PLSR) using GRAMS/386 PLSPplus version 3.02 (Galactic Industries Corp, Salem, NH) based on a one-out cross validation (7). Three types of one-out cross validations were tested. In the first, all three subsamples were used (all replicates of a sample removed during the one-out cross validation); in the second, three separate one-out cross validations were developed with only one of the three subsamples for each calibration (i.e., only the first, second, or third bags scanned); and finally, the three spectra for the subsamples were averaged to provide one spectra per sample. In addition, various subsets of the total sample population were examined. Finally, the results from the one-out cross validation were used to develop a final calibration that was then applied to the samples in question, i.e., the set used in the one-out cross validation (7, 14).

RESULTS AND DISCUSSION

Sample Composition

The results in Table 1 show the composition of the entire sample set and the final 99 samples used for calibration development. We deleted eight samples for final calibration development either because they were spectral outliers or because we found inaccuracies in the conventional assay values. The composition of the samples was diverse, with ammonium-N, total C, and total N concentrations varying by approximately 10-, 20-, and 10-fold, respectively, for the final calibration set of 99 samples. Thus, a wide range of samples from which to test the feasibility of developing NIR calibra-

Table 1. Sample composition (% fresh weight) as determined by conventional techniques.

Assay	Mean	SD	Minimum	Maximum
All manures (n = 107)				
Ammonium-N	0.18	0.08	0.02	0.47
K	0.34	0.13	0.03	0.64
Moisture	88.6	5.58	61.4	98.6
pH	7.10	0.39	6.07	8.02
P	0.20	0.10	0.04	0.86
Total C	4.61	1.94	0.46	9.17
Total N	0.44	0.16	0.09	0.94
Data set used in final calibration (n = 99)				
Ammonium-N	0.18	0.07	0.04	0.39
K	0.35	0.13	0.03	0.64
Moisture	88.7	4.39	78.3	98.6
P	0.21	0.10	0.04	0.86
Total C	4.68	1.80	0.46	9.17
Total N	0.45	0.15	0.09	0.94

tions for manure analysis was used. With the moisture content of the samples varying by 20 percentage units (final set of 99 samples), sample consistency varied from essentially that of dirty water (98.6% moisture) to that of paste (78.3% moisture).

Sample Spectra

The effect of variation in sample composition on spectra can be seen in Figure 1. Such spectral differences can make calibration development difficult because it is difficult for the PLSR process to span the wide range in spectral data found within a data set. The discontinuity in the spectra at 1098 to 1100 nm is due to the changeover in detectors at this point, and the sharp spectral features seen in the NIR portion of the spectra (1100 to 2498 nm) are often due to absorptions characteristic of the polyethylene bags (Figure 2). While effects of the discontinuity can be avoided by forcing the PLSR process to ignore it (spectral region not included in calibration), the possible effects of the polyethylene bags cannot be easily eliminated. Spectral subtraction of the bag spectra might be possible; however, variations in the bags would require that a spectrum be obtained for each bag for proper subtraction. Therefore, it was left to the PLSR process to ignore these spectral features, which have nothing in common with the constituents of interest. Previous work with silages (15), based on multiple linear regressions, demonstrated that this is a reasonable assumption. For future efforts, the design of a large, watertight cell with quartz windows may be desirable. However, unless found to produce superior calibrations, the use of such a cell would require that the cell be cleaned between samples, whereas the use of polyethylene bags avoids this problem.

Calibrations Based on All 107 Samples

The PLSR results achieved with all 107 samples and all three subsamples of each are presented in Table 2. Overall, both the one-out cross validation results and the final calibrations were quite good for total N and C and moisture, moderate for ammonium-N, and poor for K, P, and pH. The results for K and P are not surprising because neither anion has absorptions in the visible or NIR spectral ranges. Even the results shown are due to correlations between organic components in the sample and the P or K concentrations and are thus limited by the extent of such correlations. Thus, NIR has not generally been found to accurately determine such components in feed-type samples (6, 16). Coefficients of determination for K and P with total C were 0.39 and 0.32, respectively; and 0.44 and 0.21, respectively, with total N for this study. Efforts to improve the results for P and K by removing samples that were predicted particularly poorly (concentration outliers) or

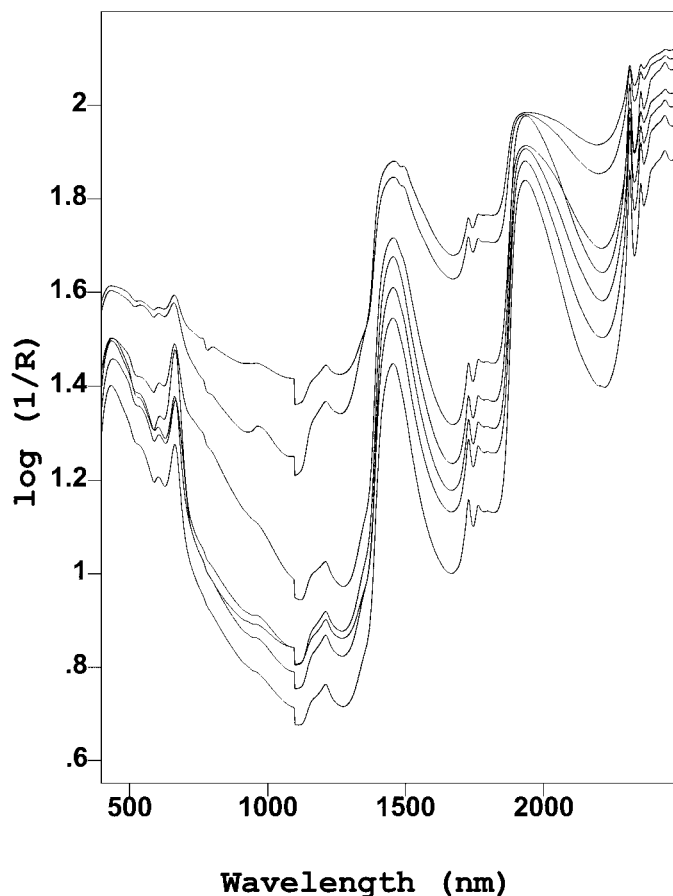


Figure 1. Spectra averaged from three subsamples of seven samples varying in moisture content: Moisture content of samples from top to bottom lines: 98.6, 95.0, 90.1, 85.4, 80.3, 71.4 and 61.4%, respectively.

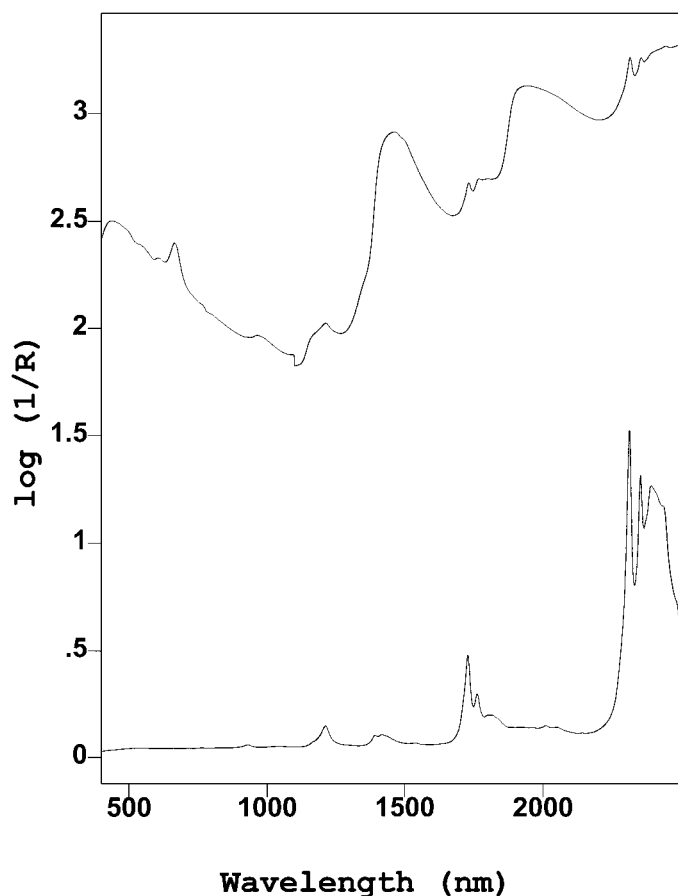


Figure 2. Spectra of a typical manure sample as scanned in a polyethylene bag (top line) and the spectra of a polyethylene bag alone (bottom line).

that were spectrally very different from the majority of the samples (spectral outliers) were not found to be helpful. For this reason, P and K will not be discussed further. Similarly, no efforts resulted in satisfactory calibrations for pH. Examination of correlations between components such as moisture and N, C, or ammo-

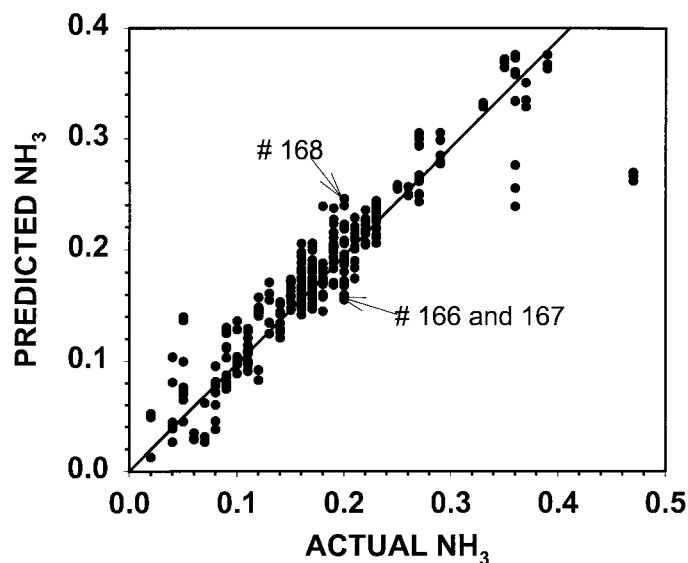


Figure 3. Predicted versus actual from one-out cross validation calibration for ammonium-N using all 321 available spectra. Samples 166 to 168 are three aliquots of the same sample. Solid line is for actual versus predicted.

num-N showed that indirect measurements could not account for the results achieved, and the highest correlation was between total C and moisture ($r^2 = 0.66$).

In contrast, the resulting calibrations for ammonium-N, moisture, and total C and N showed that the removal of relatively few samples (eight) considerably improved calibrations for all four assays. The results for the one-out cross validation for ammonium-N determination are shown in Figure 3. As shown, several samples (three subsamples per specific manure) appear to be determined much less accurately than the rest. We determined that two of the samples had poor conventional analysis results, as reflected by other work with the same samples (24), while others appeared to be spectral outliers (data not shown). Results for all four assays also showed that samples at the extremes for moisture

Table 2. Partial least squares regression results using all 107 samples and all 3 subsamples for each sample (N = 321).

Assay	Derivative ¹	# Factors	1-out cross validation		Calibration	
			R ²	RMSD ²	r ²	RMSD
Ammonium-N	2nd, g = 32	9	0.828	0.034	0.860	0.030
K	2nd, g = 8	7	0.569	0.086	0.697	0.072
Moisture	1st, g = 8	13	0.906	1.71	0.933	1.45
P	2nd, g = 16	7	0.342	0.085	0.476	0.076
pH	2nd, g = 16	9	0.573	0.256	0.662	0.228
Total C	1st, g = 8	13	0.903	0.602	0.931	0.506
Total N	1st, g = 8	10	0.900	0.051	0.920	0.046

¹Spectra mean and variance scaled and multiplicative scatter corrected, g = derivative gap in data points.

²RMSD = Root mean squared deviation = (sum squared residuals/107)^{1/2} as percentage of fresh weight.

Table 3. Partial least squares regression results using 99 samples.

Assay	Derivative ¹	# Factors	1-out cross validation		Calibration	
			R ²	RMSD ²	r ²	RMSD
Based on 3 subsamples per sample (n = 297)						
Ammonium-N	2nd, g = 32	11	0.926	0.020	0.960	0.0145
Moisture	1st, g = 16	8	0.894	1.42	0.930	1.16
Total C	1st, g = 8	9	0.903	0.560	0.940	0.439
Total N	1st, g = 8	10	0.912	0.043	0.951	0.032
Using averaged spectra (n = 99)						
Ammonium-N	2nd, g = 16	8	0.936	0.018	0.967	0.0132
Moisture	1st, g = 32	10	0.908	1.33	0.945	1.02
Total C	1st, g = 8	9	0.913	0.528	0.950	0.400
Total N	2nd, g = 16	7	0.915	0.042	0.956	0.030
Results using only 1st, 2nd, 3rd subsample in developing calibrations (N = 99)						
	1-out cross validation		Calibration			
	R ² range	RMSD range	r ² range	RMSD range		
Ammonium-N	0.908–0.927	0.0196–0.0220	0.956–0.958	0.0149–0.0152		
Moisture	0.0874–0.892	1.44–1.56	0.922–0.938	1.09–1.22		
Total C	0.886–0.901	0.569–0.606	0.939–0.960	0.356–0.441		
Total N	0.902–0.911	0.0439–0.0453	0.944–0.964	0.0274–0.0341		

¹Spectra mean and variance scaled and multiplicative scatter corrected, g = derivative gap in data points.

²RMSD = Root mean squared deviation = (sum squared residuals/99)^{1/2} as percentage of fresh weight.

content generally caused problems with calibrations, although this does not appear to be always so. Thus, while results for four out of the five samples with the highest moisture contents were consistently inaccurate, the sample with the highest moisture content was not. While further work with more samples is needed to establish firm guidelines, results with these samples suggest that samples with low solids content (<2.5%) should be handled differently. With few particles present, reflection is not the dominant spectral mode and reflectance spectroscopy does not appear to work well. For example, Malley et al. (11) have found transreflectance works well for hog manure as liquids and slurries. At the other extreme, two samples with moisture contents <72% were also inaccurately determined. While most of the samples were either slurries or at the most very pasty in consistency, these samples were very dry for dairy manures (38.6% DM for one). As a result of these findings, eight samples were removed from all further calibration studies, leaving 99 samples in the data set.

Calibration Results Using 99 Samples

The results for the 99 samples are shown in three forms (Table 3): 1) All three subsample scans were used in the calibration (n = 297); 2) the three subsample scans were averaged to give one spectrum per sample; and 3) each subsample set was used in a separate calibration (i.e.; only the 1st, 2nd, or 3rd subsample scanned was used in developing a calibration). Three

bags were scanned for each sample in an effort to determine the effects of sample nonhomogeneity. Such effects can be seen in Figure 3 for the three subsamples of manure #59 (#166, 167, and 168 on the plot). The spread in predicted ammonium-N is quite large, and residuals are both positive and negative. Unless a larger sample can be scanned, the only option is to scan more aliquots of each sample.

These results demonstrate several points: 1) Removing the eight samples from the initial set of 107 reduced the calibration errors (lower root mean squared deviation or **RMSD**) for all assays for both the one-out cross validation and the final calibrations. For the calibrations for moisture and total C and N, the number of calibration factors needed was also reduced, indicating more consistent data sets. While the number of calibration factors for ammonium-N increased, this also resulted in the greatest improvement (calibration RMSD reduced by a factor of two), indicating that a more consistent data set was achieved. 2) Averaging the three spectra available for each sample resulted in even better calibration results, with about a 9% reduction in RMSD values for the four assays. 3) Calibrations based on only a single subsample for each manure indicated that there was some variation among the subsamples. However, at maximum, calibration RMSD values were increased by only 20, 13, 10, and 13%, for moisture, ammonium-N, total C, and N, respectively, by using a single subsample over than those achieved using the average of three subsamples. Based on these results,

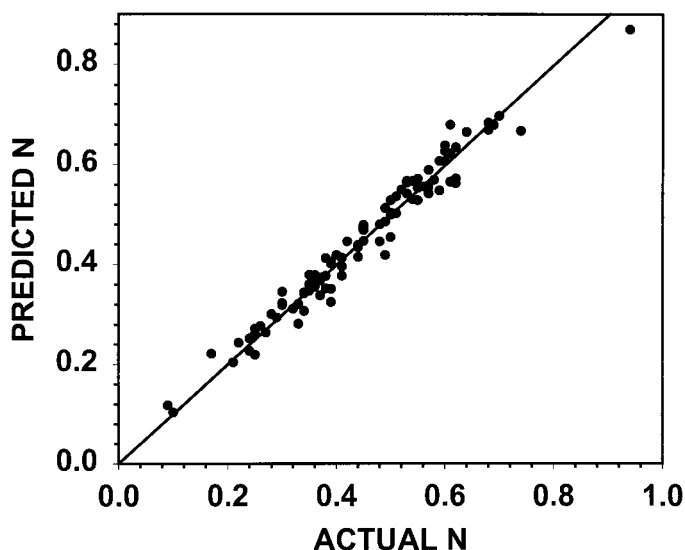


Figure 4. Calibration results for total N using the best calibration based on a single subsample for each manure ($n = 99$). Solid line is actual versus predicted.

calibrations with a single subsample were still quite satisfactory.

The differences in the final calibrations for total N achieved with the most accurate and least accurate single bag calibrations (RMSD = 0.027 and 0.034, respectively, 26% difference in error) are shown in Figures 4 and 5. Unfortunately, data from the six samples that contributed the most to this difference revealed no common factor, no sample was identified as a spectral

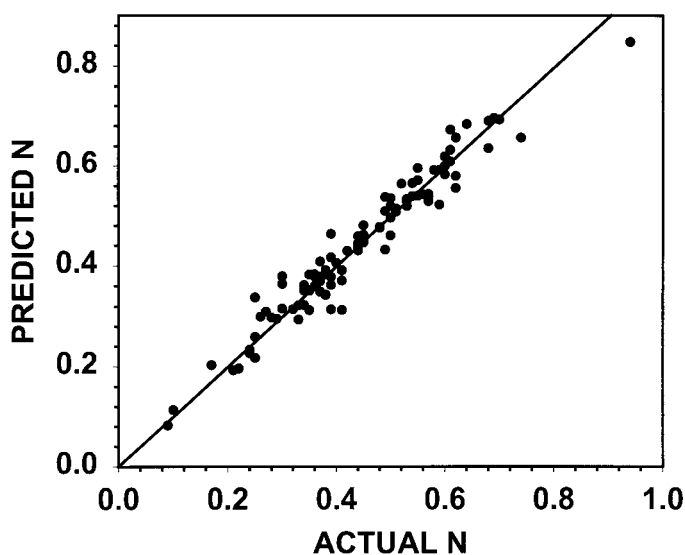


Figure 5. Calibration results for total N using the poorest calibration based on a single subsample for each manure ($n = 99$). Solid line is actual versus predicted.

outlier by the calibration program, and no samples were at the extremes in either N or moisture concentrations. Thus, no obvious way exists to identify these samples, and we must assume that a poor subsample was obtained or that something occurred during scanning. In this regard, we occasionally noticed frosting of the sample cell due to the temperature of the samples and the room humidity. Future studies should monitor this occurrence to determine whether it had any effect on accuracy. Also, samples could be rapidly warmed to an intermediate temperature or the humidity in the room could be reduced.

Although the variable nature of the samples [i.e.; cattle manure (3), hog manure (11), and composts (9) vs. dairy manure for this study] make direct comparisons with the few other published results difficult, the results for total N and total C were very similar to those found for cattle manure [r^2 of 0.934 and 0.971 for total N and C, respectively (3)]. Likewise, the results for ammonium-N were similar to those found for hog manure (r^2 of 0.97). However, the results for P and pH were much better for the hog manure than found here (r^2 of 0.99 and 0.87 for P and pH, respectively).

The results achieved with various regions of the total spectrum are shown in Table 4. The results achieved with either all available wavelengths or just the NIR portion were approximately the same, with the use of the total spectrum producing slightly better results for all but total C. However, the shorter wavelengths only (400 to 1098 nm) resulted in marked decreases in calibration accuracy for all variables and were virtually useless for determining ammonium-N. These results indicated that the development of inexpensive instruments—based on shorter wavelengths only—may not be feasible, but that filter or diode-based NIR instruments may be feasible.

Comparison of NIRS to Other Available Quick Tests for Ammonium-N

As discussed in the Introduction, several quick tests are presently marketed for determining ammonium-N in manures. Some of these are relatively inexpensive (<\$100 US for the conductivity pen) and are robust enough to be used on farm. Ammonium-N and total N were determined with six of these tests on the final set of 99 samples used in this study (24). Results showed that none of the tests produced comparable results for total N and only the Quantofix-N-Volumeter was truly comparable for ammonium-N determination ($r^2 = 0.939$, RMSD = 0.018); the reflectometer was a close second ($r^2 = 0.900$, RMSD = 0.023). Thus, NIRS not only provided equal or better results than any of the available quick tests, but also provided values for four assays in one

Table 4. Summary of best results obtained with averaged spectra (n = 99) using polyethylene bags and sample transport device.¹

Spectral region ²	Range (nm)	1-out cross validation		Calibration	
		R ²	RMSD ³	r ²	RMSD
Ammonium-N					
Visible-NIR	400–2498	0.936	0.018	0.967	0.013
NIR	1100–2498	0.940	0.018	0.956	0.015
Visible-SWNIR	400–1098	0.339	0.060	0.392	0.062
Moisture					
Visible-NIR	400–2498	0.908	1.33	0.945	1.02
NIR	1100–2498	0.895	1.41	0.916	1.27
Visible-SWNIR	400–1098	0.683	2.48	0.781	2.04
Total C					
Visible-NIR	400–2498	0.913	0.528	0.950	0.400
NIR	1100–2498	0.916	0.520	0.962	0.351
Visible-SWNIR	400–1098	0.630	1.10	0.735	0.922
Total N					
Visible-NIR	400–2498	0.915	0.042	0.956	0.030
NIR	1100–2498	0.909	0.044	0.945	0.034
Visible-SWNIR	400–1098	0.586	0.094	0.741	0.073

¹Spectra mean and variance scaled and multiplicative scatter corrected.²NIR = near-infrared, SWNIR = shortwave-NIR.³RMSD = Root mean squared deviation = (sum squared residuals/99)^{1/2} as percentage of fresh weight.

scan. Scanning a single sample would take similar or less time than most of the quick tests; however, the NIR method is much more expensive and is not practical at the present time for on-farm testing.

Finally, we tried to determine if the NIR results were based on the same sample component as the quick tests by determining if calibrations could be developed with quick test results as the reference data (data not presented), which could also be useful if a database of results with a quick test was available and one wished to compare or to add to the database in the future. NIRS could be used to reasonably determine the ammonium-N estimates by the Quantofix-N-Volumeter and reflectometer. Also, NIRS was more accurate in estimating values obtained from the quick tests, than the quick tests were in determining ammonium-N. These results are consistent with the concept that the various quick tests determine specific fractions of the N in the manures, which, while not entirely the ammonium-N or total N alone, have specific characteristics that the NIR is able to determine.

CONCLUSIONS

Results of NIR analysis of 99 diverse manures collected from dairy farms in five northeastern states demonstrated that NIRS calibrations for ammonium-N, moisture, total C, and total N can be developed and used to accurately determine the composition of dairy manures. However, results showed that NIRS cannot accurately determine K and P in dairy manures. Better

results were achieved when three subsamples of each manure were scanned, and the average spectra were used in developing calibrations, although using only a single sample for each manure also produced satisfactory results. Results from NIRS were found to be at least as, and generally more, accurate than those obtained with available quick tests.

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